

DEGRADATION OF DISLODGEABLE  
AZINPHOSMETHYL (GUTHION) RESIDUE  
ON APPLE FOLIAGE;  
EL DORADO COUNTY, 1984

By

Keith T. Maddy, Staff Toxicologist  
Susan Edmiston, Environmental Hazards Specialist III  
Dana D. Meinders, Environmental Hazards Specialist  
Don Richmond, Environmental Hazards Specialist  
Catherine Cooper, Agricultural Chemist II

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California Department of Food and Agriculture  
Division of Pest Management, Environmental  
Protection and Worker Safety  
Worker Health and Safety Unit  
1220 N Street, Sacramento, CA 95814

SUMMARY

Foliage from two treated apple orchards in the Apple Hill area of El Dorado County was sampled at predetermined times over a two month period to determine the degradation rate of azinphosmethyl (Guthion) residue and the production and degradation of its oxon analogue. Data was collected to evaluate the current 14-day reentry interval for apples required by California regulations. The insecticide was applied at the rate of 0.75 pounds of active ingredient in 300 gallons of water per acre in each orchard. Maximum mean residue was found, at one hour post-application, to be 1.02 ug/cm<sup>2</sup>. At 66 days post-application, 0.12 ug/cm<sup>2</sup> of azinphosmethyl residue, as a mean of two samples, remained in one of the two orchards. No azinphosmethyl-oxon was found in either orchard at this low application rate, even with the high ambient temperatures recorded during the study. The current reentry interval appears to provide an adequate safety margin, under the conditions encountered in this study, to protect field workers from pesticide residue-related illness.

## INTRODUCTION

Azinphosmethyl (0,0-Dimethyl-S-[(4-oxo-1,2,3-benzo-triazin-3(4H)-yl)methyl]phosphorodithioate; Guthion) is an insecticide of high acute toxicity with a wide variety of agricultural and horticultural uses in California. It provides effective pest control through its non-systemic, contact activity. Its oral LD<sub>50</sub> (rat) is most often reported to be between 11-17 mg/kg and its dermal LD<sub>50</sub> is reported to be 220 mg/kg (1). Azinphosmethyl-oxon, the oxygen analogue degradation product of azinphosmethyl, may be as much as 30 times as toxic as the parent compound (2). Azinphosmethyl is a Toxicity Category I pesticide (based on oral LD<sub>50</sub>) whose greatest known hazard to humans is believed to be acute toxicity resulting from accidental inhalation, ingestion or dermal exposure.

Agricultural field workers are protected in California from pesticide-related illness caused by dermal exposure to hazardous residues, by restricting entry into treated fields until residues remaining have reached a level calculated to be safe. This exclusion period is termed a "reentry interval". Organophosphate pesticide residues, and their corresponding oxidation products, have caused field worker illnesses in the past by reducing cholinesterase enzyme activity after significant exposure has occurred. Cholinesterase is vital for proper nervous system function.

The severity of a residue-caused field worker illness is dependent upon the quantity and toxicity of the residues present at the time of exposure and upon the extent of contact with dislodgeable foliar residue and contaminated particles from the soil (3, 4). To eliminate this hazard, safe reentry intervals were established by the California Department of Food and Agriculture (CDFA) in 1971 that were both application rate and commodity dependent (5). Reentry intervals for additional pesticides have been added since that time. For Guthion, as used on apples at the rate described in this report, the current reentry interval required in California would be 14 days.

The application of Guthion to apples in El Dorado County begins in April or early May to control codling moths and the apple maggot, as well as leafhoppers and scale insects. The formulation used in this study was a 50 percent wettable powder which is tank-mixed in water and normally applied by ground application equipment. The tank-mix may or may not include adjuvants or other pesticides. The maximum rate of Guthion for apples would be 3.125 pounds of active ingredient in up to 1,000 gallons of water per acre. Application rates at Apple Hill, El Dorado County, are normally low, however, to preserve existing beneficial insects as part of an ongoing Integrated Pest Management (IPM) plan. Guthion applications normally occur more than once per season in this area.

This field study was undertaken in the spring and summer of 1984 by the Northern Field Study Team of the Worker Health and Safety (WH&S) Unit to provide data to be used in evaluating the existing reentry restrictions for azinphosmethyl.

## METHODS

Two orchards to be treated with azinphosmethyl were located at Apple Hill through the El Dorado County Agricultural Commissioner's Office and the University of California Agricultural Extension Service Office in Placerville. Arrangements were made to monitor the first Guthion applications of the season to each orchard. On May 18th, orchard 1 was sprayed with Mobay Guthion 50% Wettable Powder (EPA Reg. No. 3125-301-AA mixed at 0.50 pound of formulated product per 100 gallons of water at 300 gallons per acre, or 0.75 pounds of active ingredient per acre. Orchard 2 was treated on May 19th with the same material at the same rate. Both applications were made with tractor-pulled orchard-fan type sprayers. The tank mix for Orchard 2 included Cyprex (1 pound/100 gallons/acre) in half the orchard and Captan (2 pounds/100 gallons/acre) in the other half. One sub-sample was collected from two separate blocks in Orchard 2.

Foliar residue samples were collected using methods as described by Gunther, et. al., (6) and Iwata, et. al., (3). Two sampling rows were selected and marked prior to application in each orchard when pre-application samples were obtained. Post-application samples were collected at pre-determined intervals and consisted of two sets of 40 leaf discs; each disc being 2.54 centimeters in diameter. One disc was punched from two "sides" of ten sampled trees at each sampled row. All samples were collected from a height of approximately two meters in clean glass jars which were subsequently sealed with foil-lined lids. Samples were kept on ice and delivered for analysis as quickly as possible after collection.

The determination of dislodgeable foliar azinphosmethyl and azinphosmethyl-oxon residue levels was accomplished by the Worker Health and Safety Laboratory in Sacramento. Residues were extracted from the leaf disc surfaces in a water/Sur-ten solution. Accumulated water was then extracted with dichloromethane and evaporated. Known volume solutions were made with ethyl acetate and analyzed by gas/liquid chromatography. Detailed explanations of methods and equipment conditions have been given in several other HS Reports.

## RESULTS AND CONCLUSIONS

Mean levels of dislodgeable foliar azinphosmethyl residue found in each orchard are reported in Table 1. Weather and air quality records for the study period were obtained for the closest monitoring station to the study area and are listed in Table 2. Figure 1 illustrates the mean degradation rate of azinphosmethyl over time after application to apples.

Under the conditions encountered in this study, levels of azinphosmethyl residue did not exceed a calculated safe level of foliar residue published by Knaak, et. al., as  $1.60 \text{ ug/cm}^2$  (7). The maximum mean azinphosmethyl residue level found was in Orchard 1 five hours after application at  $1.02 \text{ ug/cm}^2$ . No azinphosmethyl-oxon was found during the study even under the high temperatures reported for the study period; 31 of 67 days (46%) had maximum temperatures of  $90^\circ\text{F}$  or above. The current reentry interval of 14 days would appear to provide adequate field worker protection under the conditions observed in this study, unless potential exposure during work activities is underestimated or if the calculated safe level has been

overestimated. The degradation rate revealed in this report indicates that for Guthion, applied to apples at the rates used here, a 14-day reentry interval might be excessive.

Addendum 1 reports residue levels found after a second Guthion application to one of the orchards monitored for this report.

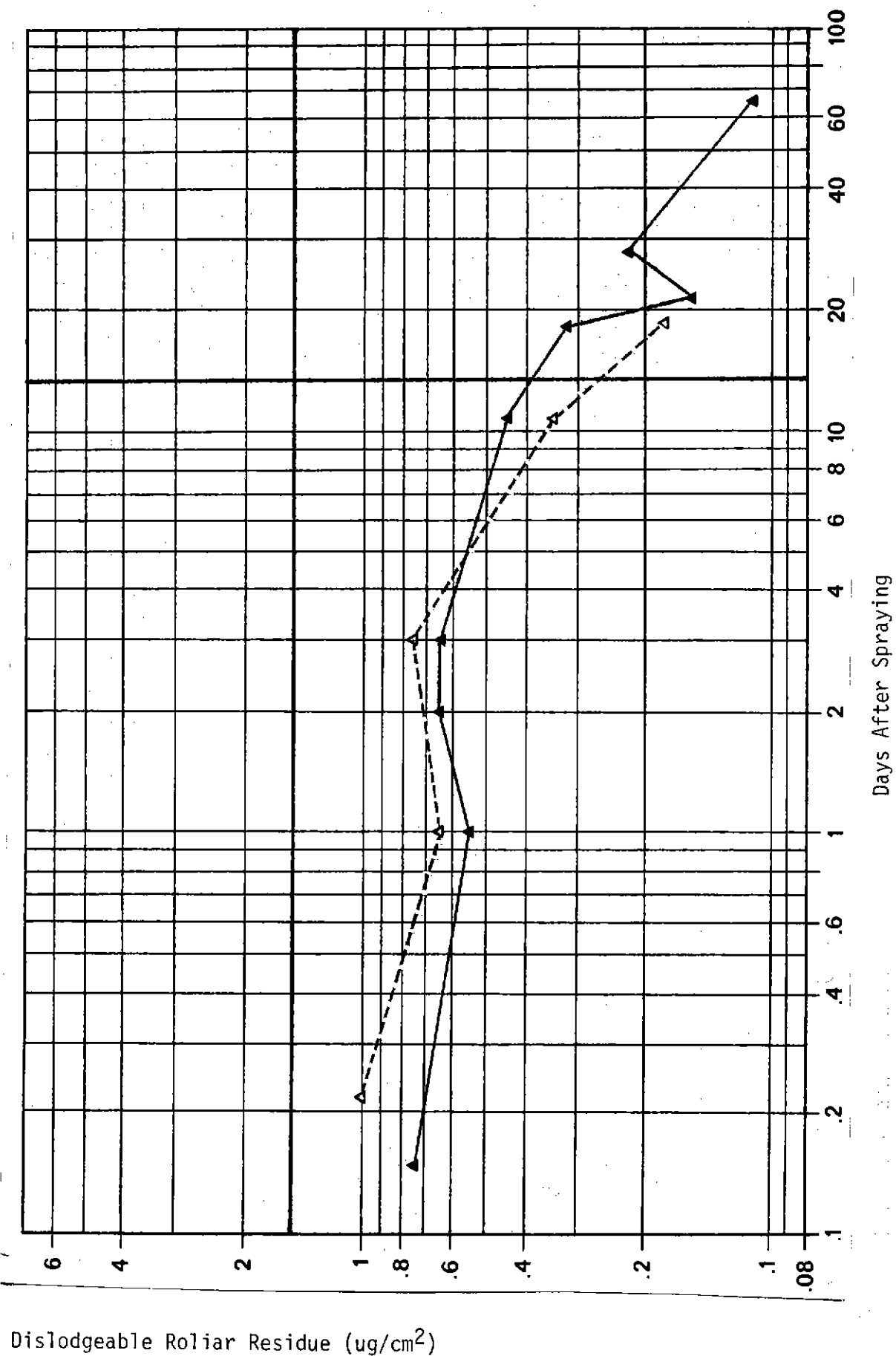


Figure 1 - Mean value degradation for foliar dislodgeable azinphosmethyl residue on apples in Orchard 1 (open symbols) and Orchard 2 (closed symbols). The heavy horizontal line at 1.6 ug/cm² is the calculated safe level. The heavy vertical line at 14 days is the current reentry interval.

TABLE I. Mean Levels of Dislodgeable  
Azinphosmethyl Residue After Guthion  
Application to Apples, in ug/cm<sup>2</sup>

<u>Orchard</u>	<u>Pre- Sample</u>	<u>2 Hours Post</u>	<u>5 Hours Post</u>	<u>24 Hours</u>	<u>48 Hours</u>	<u>72 Hours</u>	<u>11 Days</u>	<u>17 Days</u>	<u>22 Days</u>	<u>27 Days</u>	<u>66 Days</u>
1	ND*	NS**	1.02	.65	NS	.86	.35	.19	NS	NS	NS
2	ND	.75	NS	.55	.64	.47	.54	.47	.16	.23	.12
Overall Mean	--	.75	1.02	.60	.64	.67	.45	.33	.16	.23	.12

\*ND - None detected at or above the minimum detectable level of 0.012  
ug/cm<sup>2</sup>.

\*\*NS - No sample collected.

TABLE II. Climatological and Air  
Quality Data Collected for  
the Sampling Period

<u>Month</u>	<u>Days</u>	<u>Temperature (°F)</u>			<u>Rainfall (inches)</u>	<u>Oxidant Levels</u>
		<u>Max.</u>	<u>Min.</u>	<u>Mean</u>		
May	13	86.1	61.8	74.0	30th = Trace	To be added
June	30	82.5	57.9	70.2	4th = .57 5th = .05 6th = .30 7th = .02	
July	24	93.6	67.9	80.8	17th = Trace 23rd = Trace	
Overall	67	87.4	62.5	75.0		

Weather data from the National Weather Service reported by the Institute of  
Forest Genetics, Camino, CA.

## ADDENDUM 1

A second application of Guthion was made to Orchard 2, 67 days after the first. Leaf disc samples were again collected as in the attached study in order to evaluate the effects of multiple applications of Guthion. Levels of azinphosmethyl foliar residue found are reported here; however, while the application rate remained the same, only one sample row received Guthion while the second was treated with carbaryl to maintain resistant beneficial insects. Sub-samples were collected as before from the same two sample rows so that one sample row reflected additional azinphosmethyl while the second contributed only residue from the first application. Actual levels of azinphosmethyl are reported in Table A-1.

Due to miscommunication with the orchard owner, an adjustment was not made in response to the changed application, so that sample results should reflect approximately one-half of the azinphosmethyl present after the second application. Doubling the mean would give a closer estimate of true levels of residue remaining, but no judgments should be drawn from this data. It is included here only to document the use of multiple applications and the Northern Field Team's attempt to monitor such a situation and to credit the Laboratory's efforts in processing the samples. Monitoring of a multiple application spray program using a single pesticide such as Guthion should still be a goal of the Worker Health and Safety Unit in order to understand the additive effects of such a spray program.

TABLE A-1 - Actual Levels of Dislodgeable Azinphosmethyl Residue After a Second Guthion Application to Orchard 2 in ug/cm<sup>2</sup>

[illegible]

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